

# Compositional tuning of ALD MgZnO for Thin Film Transistors

J.S. Wrench, I.F. Brunell and P. R. Chalker

*School of Engineering, Centre for Materials and Structures, University of Liverpool, L69 3GH, United Kingdom*

J. Jin, A. Shaw, I. Mitrovic and S. Hall

*Department of Electrical Engineering and Electronics, University of Liverpool, L69 3GJ, United Kingdom*

## Abstract

Thin film transistors have been fabricated using magnesium zinc oxide layers deposited by atomic layer deposition at 200°C. The composition of the MgZnO is systematically modified by varying the ratio of MgO and ZnO deposition cycles. A blue-shift of the near band-edge photoluminescence after post-deposition annealing at 300°C indicates significant activation of the Mg dopant. A 7:1 ratio of ZnO : MgO deposition cycles was used to fabricate a device with a TFT channel width (W) of 2000  $\mu\text{m}$  and a channel length (L) of 60  $\mu\text{m}$ . This transistor yielded a saturation mobility of 4  $\text{cm}^2/\text{V s}$  and a threshold voltage of 7 V respectively. The on/off ratio was  $1.6 \times 10^6$  and the maximum interface state density at the ZnO/SiO<sub>2</sub> interface of  $\sim 6 \times 10^{12} \text{cm}^{-2}$ .

**Keywords:** Thin Film Transistor, Magnesium Zinc Oxide, ALD

Zinc oxide (ZnO) - based thin film transistors (TFTs) are attractive candidates for transparent electronics. Conventional TFT materials, such as hydrogenated amorphous silicon (a-Si:H), benefit from ambient deposition conditions and ease of processing. However they are criticised because of their relatively small mobility ( $\mu_{\text{eff}} < 1 \text{ cm}^2/\text{Vs}$ ) [1], which is too low for high-speed switching in flat

panel displays, especially for 3D and high-resolution large-area displays which require high refreshing rates. As an alternative, RF-sputtered magnesium zinc oxide (MgZnO) has been explored as a TFT material [2]. The benefits of adding Mg to ZnO are cited as a larger band gap ( $E_g$  MgO 7.7eV, ZnO 3.28eV) and lower oxygen-related defect concentrations because of the higher oxygen-affinity of magnesium. This view is substantiated by Ku et. al. [3] who have used metal–organic chemical vapor deposition to deposit  $Mg_{0.06}Zn_{0.94}O$  as an active layer in TFTs with superior thermal stability compared to pure ZnO devices. In this paper, we use atomic layer deposition (ALD) to deposit MgZnO channels in TFTs. ALD has become a mainstream process for the manufacture of high- $\kappa$  dielectrics in silicon electronic devices and elsewhere. For example ALD has been used to deposit  $Mg_{1-x}Zn_xO$  films which been investigated for use as buffer layers in  $Cu(In,Ga)Se_2$  - based solar cells [4]. The  $Mg_{1-x}Zn_xO$  films were grown using diethyl zinc (DEZn), bis(cyclopentadienyl) magnesium ( $Mg(CpEt)_2$ ) and water as precursors in the temperature range from 105 to 180°C. Single-phase ZnO-like films were obtained for  $x < 0.2$ , followed by a two-phase region of ZnO- and MgO-like structures for higher Mg concentrations. Increasing optical band gaps of up to above 3.8 eV were obtained for  $Mg_{1-x}Zn_xO$  with increasing  $x$ . In this paper, we report the use of ALD to fabricate a range of  $Mg_{1-x}Zn_xO$  thin film transistors and the influence that composition has on the material and device characteristics.

The atomic layer deposition experiments were performed using the liquid DEZn and bis(ethylcyclopentadienyl)magnesium,  $Mg(CpEt)_2$  sources, which were delivered, at room temperature and 95°C respectively, into the process chamber from independent sources. The  $Mg_{1-x}Zn_xO$  films are deposited using  $x$  cycles of ZnO steps, via exposure of the surface to successive steps of DEZn and then water vapour. Intermittent pump purge steps are used to prevent gas-phase pre-reaction, which ensures the surface reaction. After the  $x$  ZnO cycles, a single MgO cycle is deposited, via exposure of the surface to successive steps of  $Cp_2Mg$  and then water vapour. The ratio of DEZn :  $Cp_2Mg$  ALD cycles were tested for 2:1, 3:1, 5:1, 7:1, 8:1, 9:1, 10:1, 20:1 and 99:1.

Crystallographic characterisation of the  $\text{Mg}_{1-x}\text{Zn}_x\text{O}$  films was performed using X-ray diffraction (XRD) and room temperature photoluminescence (PL) spectroscopy. The films were deposited on glass substrates at  $200^\circ\text{C}$  and were subsequently annealed at  $300^\circ\text{C}$  in air for one hour. The crystalline phases were identified by XRD using  $\text{Cu K}\alpha$  radiation ( $0.154051\text{ nm}$ ,  $40\text{ kV}$ ,  $50\text{ mA}$ ) and diffraction patterns from a sample of the annealed films is shown in Fig. 1(a). The crystalline texture of the films undergoes some significant changes across the composition range studied. As the Mg incorporation increases from 49:1 to 7:1 the c-axis (002) oriented growth diminishes, which is indicated by the decreasing ratio of the (002) diffraction peak with respect to the (100) and (101) peaks. Notably, the full-width at half maxima (FWHM) of the diffraction peaks remains unchanged, suggesting that the crystalline domain size fairly constant. PL data were excited using  $325\text{ nm}$  ( $3.82\text{ eV}$ ) excitation from a He-Cd laser. Spectra were acquired using a Raman confocal microscope set to  $100\mu\text{m}$  aperture coupled to a single grating spectrometer equipped with a notch filter and a CCD camera detector. The PL spectra acquired from a 7:1  $\text{Mg}_{1-x}\text{Zn}_x\text{O}$  film deposited at  $200^\circ\text{C}$  on glass is shown in Fig. 1(b). The as-deposited film exhibits a peak emission at  $3.41\text{ eV}$  and is attributed to near band-edge emission arising from the recombination of free excitons. The film was subsequently annealed at  $300^\circ\text{C}$  in air for one hour and the PL spectrum from this film was observed to blue-shift to  $3.51\text{ eV}$ . The band gap of  $\text{Mg}_{1-x}\text{Zn}_x\text{O}$  alloys is known to increase with [Mg] content via the Burstein-Moss effect [5, 6], in which magnesium-induced charge carriers occupy states just above the bottom of the ZnO conduction band. This has the effect of pushing the absorption edge to higher energies. The same effect has been observed in gallium-doped ZnO deposited by ALD [7]. In the present case, the blue-shift effect is ascribed to the increased activation of the Mg dopant from the deposition temperature at  $200^\circ\text{C}$  to the higher  $300^\circ\text{C}$  annealing.

$\text{Mg}_{1-x}\text{Zn}_x\text{O}$  films were grown at  $200^\circ\text{C}$  via the atomic layer deposition (ALD) technique on a highly doped n-type silicon wafer with a  $50\text{ nm}$  thermally oxidised  $\text{SiO}_2$  layer which served as a gate

dielectric for the TFT. The Mg doped films were grown to a thickness of 50 nm where the cycle ratio between the ZnO and Mg precursors ranged from 10:1 to 2:1. Source/drain electrodes with a thickness of 100 nm were fabricated by evaporating aluminium through a shadow mask, which defined a TFT channel width (W) of 2000  $\mu\text{m}$  and a channel length (L) of 60  $\mu\text{m}$ . Finally, the devices were subjected to the same thermal annealing process used for the samples above. A schematic of the fabricated bottom-gated ZnO TFTs is shown in the inset of Fig. 2 (b). The electrical characteristics of ZnO TFTs were measured at room temperature in the dark using an Agilent B1500 semiconductor parameter analyser. Fig. 2 shows a range of characteristics for MgZnO TFTs as a function of the percentage of Mg ALD doping cycle. Fig. 2(a) and (b) show the field effect mobility in the saturation region and threshold voltage which were extracted using the standard equation for source-drain saturation current:

$$I_{DS} = \frac{C_i \mu_{SAT} W}{2L} (V_{GS} - V_T)^2 \text{ for } V_{DS} > V_{GS} - V_T \quad (1)$$

where  $C_i$  is the gate capacitance per unit area,  $\mu_{SAT}$  is the mobility in the saturation region,  $V_{GS}$  is the gate voltage referenced to the source and  $V_T$  is the threshold voltage. The mobility in the saturation region shows a tendency to decrease from 4.32 to 0.47  $\text{cm}^2/\text{V s}$  as the magnesium content increases across the doping cycle range from 0.09 (10:1) to 0.33 (2:1). The FWHM of the X-ray diffraction data for these films indicates an approximately constant grain size, which suggests that impurity scattering rather than grain boundary scattering has some influence in these thin channel materials, although the effect of increased electron effective mass due to band-gap widening may not be neglected. The threshold voltage for the devices exhibits the opposite trend increasing from 6.05V to 9.51V respectively. The variation of on/off ratio with magnesium content shown in Fig 2(c) and exhibits a maximum at a doping cycle fraction of 7:1. From the transfer characteristics, the sub-threshold swing (S) can be extracted using the equation

$$S = \frac{dV_{GS}}{d(\log I_{DS})}. \quad (2)$$

where the sub-threshold swing can be obtained from the experimental characteristics. From  $S$  the maximum density of surface state ( $N_{it}$ ) at the channel/dielectric interface can be estimated using the following equation.

$$N_{it} = \left[ \frac{S \log(e)}{(kT/q)} - 1 \right] \frac{C_i}{q} \quad (3)$$

where  $k$  is Boltzmann's constant,  $e$  is the base of the natural logarithm,  $T$  is the absolute temperature and  $q$  is the electron charge. The variation in the interface state density ( $N_{it}$ ) at the MgZnO/SiO<sub>2</sub> interface for the doping range investigated is shown in Fig 2(d) and a minimum was observed for the 7:1 composition. This observation is contrary to the interface state densities reported for RF co-sputtered MgZnO TFTs [8] deposited onto SiO<sub>2</sub>/n+-Si substrates at 300°C. In that study it was found that the addition of magnesium generally increased  $N_{it}$ . This can be explained by the ALD doping mechanism in which the doped ZnO interface with the underlying SiO<sub>2</sub> is predominantly ZnO-like. From the parameters presented in Fig. 2, it is apparent that the optimum TFT performance, in terms of on/off ratio, was achieved for the Zn:Mg (7:1) composition. Fig. 3 shows (a) the output and (b) the transfer characteristics for a typical MgZnO TFT fabricated using the 7:1 process. This TFT operates as an  $n$ -channel, enhancement-mode device where there is good saturation at high drain bias. The mobility in the saturation region and the threshold voltage obtained for the device were 4 cm<sup>2</sup>/V s and 7.1 V respectively. The on/off ratio was observed to be  $1.6 \times 10^6$  and the maximum interface state density at the ZnO/SiO<sub>2</sub> interface of  $\sim 6.49 \times 10^{12} \text{ cm}^{-2}$ .

Atomic layer deposition has been used to deposit the TFT channel using a range of Mg<sub>1-x</sub>Zn<sub>x</sub>O compositions. The doping was controlled, by varying the ratio of deposition cycles for ZnO and MgO, from diethyl zinc and bis(ethylcyclopentadienyl)magnesium with water vapour as the oxidant. Post deposition annealing at 300°C in air, was observed to blue-shift the photoluminescence near band edge emission, which was ascribed to the activation of the magnesium dopant. The magnesium content within the films influenced the saturation mobility,

threshold voltage, on/off ratio and interface state density. The optimum TFT performance, in terms of on/off ratio, was achieved for the Zn:Mg (7:1) composition.

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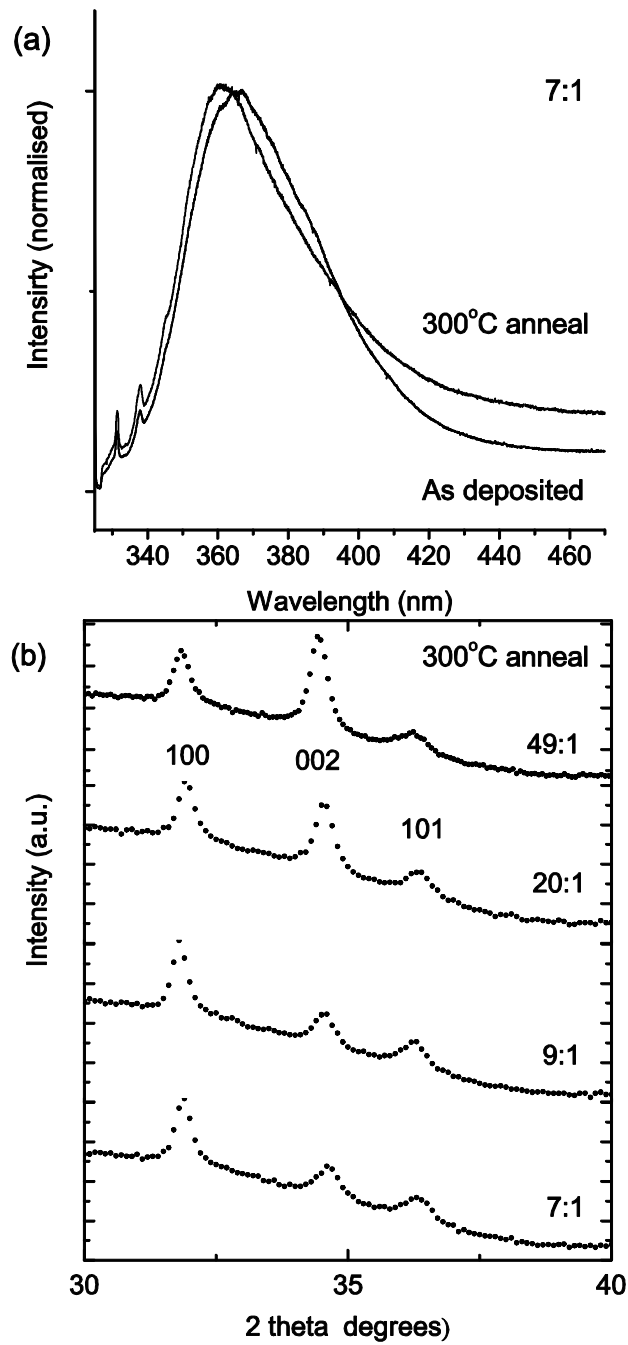


Figure 1. (a) UV photoluminescence and (b) X-ray diffraction patterns of Mg:ZnO deposited using varying Mg doping cycle ratios.

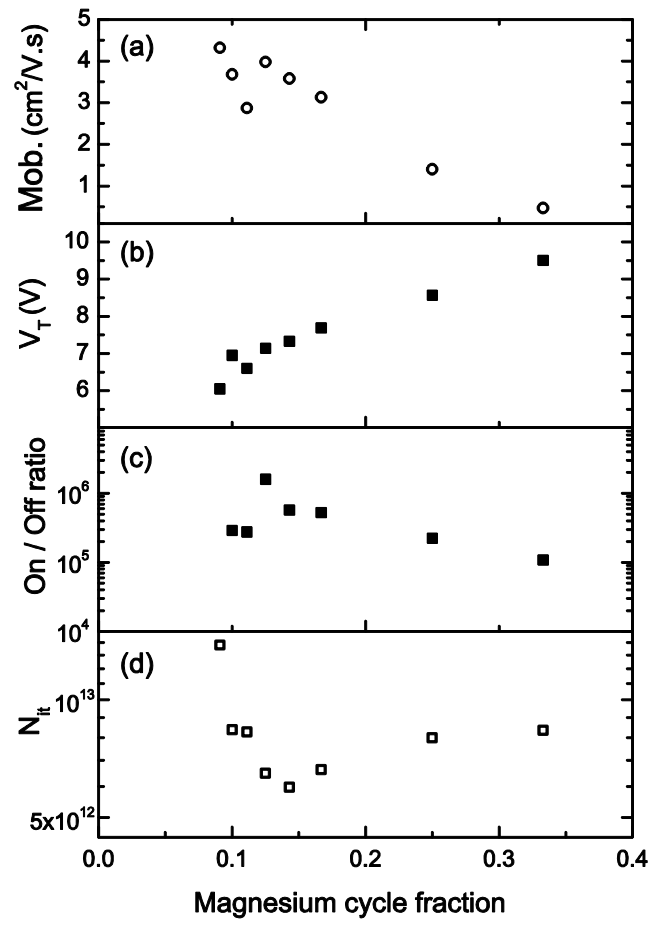


Fig 2. Characteristics of TFTs with varying Mg doping cycle fraction. (a) Saturation field-effect mobility, (b) threshold voltage, (c) On/Off ratio and (d) Interface trap density.



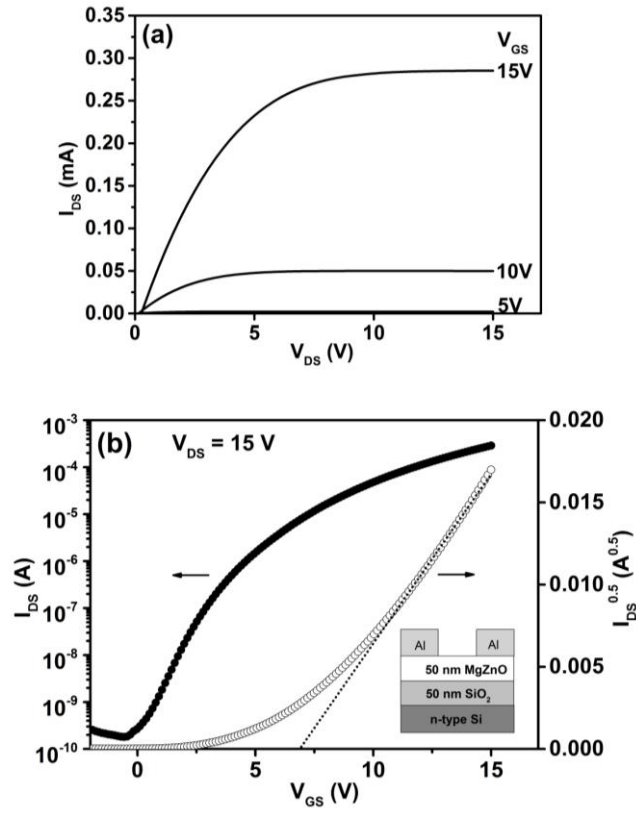


Fig. 3. (a) Output and (b) transfer characteristics of an 7:1 ALD Mg doped ZnO TFT. Square root of drain current and a linear fit (dashed line) are also shown in (b). The inset shows a schematic of the ZnO TFTs.